

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in and relating to Suspensions of Polymeric Chlorotrifluoroethylene

We, THE BRITISH THOMSON-HOUSTON COMPANY LIMITED, a British Company having its registered office at Crown House, Aldwych, London, W.C.2, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- 10 This invention is concerned with suspensions of polymeric chlorotrifluoroethylene. More particularly, the invention relates to a suspension comprising (1) a dispersed phase of finely divided solid polymeric chlorotrifluoroethylene and (2) a dispersing medium comprising (a) an organic liquid mixture which includes a low polymer of chlorotrifluoroethylene and which, at elevated temperatures but below the boiling point of the liquid, is a solvent for the aforementioned polymer, and (b) a liquid diluent which is a non-solvent for the polymer at any temperature and which is an oxygen-containing compound having a boiling point above 50° C. and selected from the class consisting of saturated aliphatic ethers (both straight-chained and cyclic), saturated aliphatic monohydric alcohols (including halogenated, e.g., chlorinated alcohols), aliphatic ketones, aliphatic esters, aliphatic lactones, aliphatic acetals, mixtures of monohydric saturated aliphatic alcohols and dihydric saturated aliphatic alcohols, and mixtures of all the foregoing oxygen-containing compounds. The invention also embraces methods for making the above-described suspensions.

Polymeric chlorotrifluoroethylene has been found to have good heat resistance and chemical resistance and because of this is eminently suitable for many applications where such properties are desired. Electrical conductors insulated with polymeric chlorotrifluoroethylene are capable of withstanding temperatures of the order of from about 150° to 200° C. for long periods of time with little

change in the physical characteristics or of the insulating properties of the polymeric insulation. Such polymeric material is also highly desired for many applications where its high softening point is an advantage. Thus, it is possible to mould various objects from the polymeric chlorotrifluoroethylene, either with or without fillers, to give useful articles which are dimensionally stable over a wide temperature range.

Because of its extreme chemical resistance and substantial insolubility in many of the common organic solvents, great difficulty has been experienced in obtaining the polymeric chlorotrifluoroethylene in usable form whereby it can be employed for coating or impregnating applications. Many attempts have been made to form solutions of the polymeric chlorotrifluoroethylene, but these attempts have generally been unsuccessful because the limit of solubility of the polymeric chlorotrifluoroethylene in the solvent has been so small as to render it impractical. Attempts to prepare suspensions of polymeric chlorotrifluoroethylene have also been generally unsuccessful because of the poor stability of such suspensions in the dispersing mediums employed heretofore with polymeric chlorotrifluoroethylene.

We have now discovered for the first time it is possible to make relatively stable suspensions of polymeric chlorotrifluoroethylene (any solid polymer thereof may be employed) using as the suspending medium a mixture of liquids described above in the first paragraph of this application. This is done by first grinding the polymeric material, for instance, in a micro-pulverizer, to a fine particle size and thereafter mixing the finely divided polymer with a dispersing phase comprising a mixture of ingredients comprising (a) an organic liquid which is a solvent for the polymer at an elevated temperature but below the boiling point of the liquid and (b) an oxygen-containing compound selected from the class described

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previously, and finally grinding this mixture, for example, in a pebble mill or a ball mill for a time sufficient to yield a stable, uniform suspension.

5 Suspensions made in accordance with our above-described method are uniformly stable over long periods of time. We are able to prepare by our method smooth, creamy suspensions which can be obtained in two to three
10 days' grinding time in standard ball mills and which are more uniform, less granular, less thixotropic, and have slower settling rates than those obtained from many other types of organic liquids. If there should be
15 some slight settling out of the suspended polymeric material, it is possible by mere stirring, either before use or during use, to reinstate the suspension to its former acceptable state. Although some dispersions of
20 similar polymers, e.g., polymeric tetrafluoroethylene, have been made using other materials as a dispersing phase, nevertheless, attempts to use these particular dispersing media with polymeric chlorotrifluoroethylene have been
25 generally unsuccessful.

Generally, the procedure followed for making our suspensions comprises pulverizing or grinding polymeric chlorotrifluoroethylene to a fine particle size of the order of about 0.2
30 to 25 microns, preferably 0.5 to 15 microns. This may be accomplished by grinding the polymer in a micropulverizer used for such purposes. Thereafter, the finely ground polymer and the mixture of liquids comprising
35 the dispersing phase are mixed together and again ground, this time, for instance, in either a ball mill or a pebble mill. The ratio by weight, of dispersing phase and finely divided polymer may be varied within wide
40 limits depending upon the desired concentration of the final suspension. Thus, we may advantageously employ, by weight, from 0.01 to 1 or more parts of the polymer per part of the liquid dispersing phase. A range which
45 we have found useful comprises, by weight, from about 0.05 to 0.3 part polymer per part of the liquid dispersing phase. On a percentage basis, good results may be realized when the polymer comprises about 10 to 30 per
50 cent., by weight, of the total weight of polymer and the dispersing phase.

From the foregoing general description it will be apparent that our invention employs both an active solvent and a relatively cheap,
55 non-solvent, diluent, thus permitting a considerable saving in money. The use of a dispersing phase comprising a mixture of ingredients wherein one of the ingredients is a solvent for the polymer at elevated temperatures, has several advantages. In the first place,
60 by using a relatively volatile non-solvent diluent in the dispersing phase, this diluent flashes off first during the baking cycle when the coated object is passed through a baking
65 oven at elevated temperatures to effect fusion

or coalescence of the individual particle of polymeric chlorotrifluoroethylene deposited on the surface. The active solvent or solvents remaining in the dispersing phase are then able
70 to dissolve or partially dissolve or to plasticize or swell the uniformly deposited, finely divided particles of solid, polymeric chlorotrifluoroethylene. Sintering or fusion, therefore, of the individual polymeric particles occurs at
75 temperatures lower than are normally required for the pure polymer. After fusion, the active solvents are preferably completely removed by further heating. The active (i.e. solvents in which the polymer is soluble at elevated temperatures) higher boiling solvents can be
80 recovered by means of a suitable recovery system and retained for use in making additional suspensions.

The proportion of active solvent in the dispersing phase may, of course, be varied within
85 wide limits. However, for economical reasons we have found it practical to use a minor proportion (e.g., from 5 to 49 per cent., by weight, for instance, from 10 to 40 per cent., based on the total weight of the dispersing
90 phase) of such liquids and a major proportion (e.g., from 51 to 95 per cent., by weight) of the liquid non-solvent (i.e., for the polymeric chlorotrifluoroethylene) diluent. Variations within these ranges, e.g., from 5 to 90 per
95 cent. of the active solvent and from 10 to 95 per cent. of the non-solvent diluent, may be employed without departing from the scope of the invention.

The number of liquid active solvents or
100 mixture of such materials which we have found can be employed in the practice of this invention are relatively few. Among these may be mentioned, for example, certain alkylated, preferably liquid, aromatic hydrocarbons, for
105 instance, pseudocumene, mesitylene, *t*-butylbenzene, beta-methylnaphthalene, para-*t*-butyltoluene, alpha-beta-dimethylnaphthalene, amylbiphenyl, alpha-methyl, para-methylstyrene, para-cymene, distyrene (styrene
110 dimer), diamylbiphenyl, para-di-*t*-butylbenzene; certain high boiling organic esters, for instance, dibutyl phthalate, dibutyl sebacate, butyl stearate, dibutyl adipate, dioctyl sebacate, methyl stearate, tributyl
115 citrate, tributyl tricarballylate, acetyl tributyl citrate, dihexyl tetrachlorophthalate, dioctyl tetrachlorophthalate (including its isomers, e.g., di-(2-ethylhexyl) tetrachlorophthalate), triethylene glycol di-(2-ethylhexoate), beta-
120 naphthyl benzoate, and mixtures thereof, fluorinated organic compounds having a boiling point above 110° C. and selected from the class consisting of (a) nucleary fluorinated aromatic hydrocarbons containing two aromatic
125 nuclei free of other substituents, (b) halogenated (e.g., chlorinated, brominated) derivatives of lower alkyl-substituted (e.g., methyl, ethyl, propyl, isopropyl and butyl) aromatic hydrocarbons containing fluorine (e.g., from 1
130

- to 6 or more fluorines) in the alkyl substituent, (c) fluorinated-chlorinated aliphatic hydrocarbons of the C₃ and C₄ series containing at least two chlorine atoms (e.g., from 2 to 6).
- 5 Suitable low polymers of chlorotrifluoroethylene would be liquid low molecular weight polymers of chlorotrifluoroethylene having the recurring structural unit (CF₂—CFCl)_n where n is an integer equal to from 4 to 16, inclusive.
- 10 Mixtures of the foregoing materials may also be employed as will be apparent to those skilled in the art.

Additional examples of the active solvents which may be employed in the practice of our invention may be found in our co-pending Application No. 26763/50 (Serial No. 676,597).

In order that those skilled in the art may better understand how the present invention

may be practised, the following compositions 20 are given by way of illustration and not by way of limitation. All parts are by weight.

EXAMPLE.

In this example polymeric chlorotrifluoroethylene (of different no strength tempera- 25 tures) in a finely divided form wherein the average particle size was from about 0.5 to 5 microns was mixed with a liquid dispersing medium comprising a mixture of organic liquids of which a major proportion were non- 30 solvents for the polymer and a minor proportion were solvents for the polymer at elevated temperatures. The following table shows the ingredients employed in making the suspen- 35 sions as well as the proportions of ingredients and the time the mixture of ingredients was milled to obtain the suspensions.

Ingredients	Parts by weight	Time, minutes
1. Polymeric chlorotrifluoroethylene (M.W. 100,000)	100	10
2. Carbon tetrachloride	100	10
3. Chloroform	100	10
4. Methylene chloride	100	10
5. Ethyl chloride	100	10
6. Ethyl bromide	100	10
7. Ethyl iodide	100	10
8. Propyl chloride	100	10
9. Propyl bromide	100	10
10. Propyl iodide	100	10
11. Butyl chloride	100	10
12. Butyl bromide	100	10
13. Butyl iodide	100	10
14. Pentyl chloride	100	10
15. Pentyl bromide	100	10
16. Pentyl iodide	100	10
17. Hexyl chloride	100	10
18. Hexyl bromide	100	10
19. Hexyl iodide	100	10
20. Heptyl chloride	100	10
21. Heptyl bromide	100	10
22. Heptyl iodide	100	10
23. Octyl chloride	100	10
24. Octyl bromide	100	10
25. Octyl iodide	100	10
26. Nonyl chloride	100	10
27. Nonyl bromide	100	10
28. Nonyl iodide	100	10
29. Decyl chloride	100	10
30. Decyl bromide	100	10
31. Decyl iodide	100	10
32. Undecyl chloride	100	10
33. Undecyl bromide	100	10
34. Undecyl iodide	100	10
35. Dodecyl chloride	100	10
36. Dodecyl bromide	100	10
37. Dodecyl iodide	100	10
38. Tridecyl chloride	100	10
39. Tridecyl bromide	100	10
40. Tridecyl iodide	100	10
41. Tetradecyl chloride	100	10
42. Tetradecyl bromide	100	10
43. Tetradecyl iodide	100	10
44. Pentadecyl chloride	100	10
45. Pentadecyl bromide	100	10
46. Pentadecyl iodide	100	10
47. Hexadecyl chloride	100	10
48. Hexadecyl bromide	100	10
49. Hexadecyl iodide	100	10
50. Heptadecyl chloride	100	10
51. Heptadecyl bromide	100	10
52. Heptadecyl iodide	100	10
53. Octadecyl chloride	100	10
54. Octadecyl bromide	100	10
55. Octadecyl iodide	100	10
56. Nonadecyl chloride	100	10
57. Nonadecyl bromide	100	10
58. Nonadecyl iodide	100	10
59. Eicosyl chloride	100	10
60. Eicosyl bromide	100	10
61. Eicosyl iodide	100	10

TABLE I.

5	Suspension No.	Weight Polymer Parts	Dispersing Phase	Weight of Dispersing Phase Components Parts	Milling Time Days
	1	175	^a Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	98 147 580	3
10	2	175	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	140 210 475	4.7
	3	175	Fluorolube alpha-Chloronaphthalene <i>n</i> -Butanol	98 147 580	3
15	4	175	Fluorolube Mesitylene <i>n</i> -Butanol	98 147 580	3
	5	175	Fluorolube ^a Solvesso 150 <i>n</i> -Butanol	98 147 580	3
20	6	^a 175	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	98 147 580	5
	7	^a 165	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	132 199 504	5.7
	8	^a 180	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	140 205 475	10
30	9	^a 175	Fluorolube alpha-Chloronaphthalene <i>n</i> -Butanol	98 147 580	5
	10	^a 180	Fluorolube alpha-Chloronaphthalene <i>n</i> -Butanol	131 197 492	6.7
35	11	^a 175	Fluorolube Mesitylene <i>n</i> -Butanol	98 147 580	5
40	12	^a 160	Fluorolube Hexachlorobutadiene <i>n</i> -Butanol	90 135 615	5
	13	^a 165	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Hexanol	132 199 504	4
45	14	^a 165	Fluorolube alpha-Fluoronaphthalene 2-Ethylhexanol	132 199 504	4
	15	^b 165	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	132 199 504	5.7
50	16	^b 175	Fluorolube Mesitylene <i>n</i> -Butanol	98 147 580	5
	17	^b 150	Fluorolube <i>t</i> -Butyl benzene <i>n</i> -Butanol	100 150 600	4.8
	18	^c 300	Fluorolube alpha-Fluoronaphthalene <i>n</i> -Butanol	111 167 422	3
60					

The polymer employed in Suspension Nos. 1 to 5 had a no strength temperature of about 245° C.

^aNo strength temperature of about 270° C.

^bNo strength temperature of about 305° C.

^cThis polymer was more finely divided than any of the three other polymers employed above and had a no strength temperature of about 220° C.

^dLow molecular weight polymer of chlorotrifluoroethylene and more particularly described in copending Application No. 26763/50 (Serial No. 676,597).

^eThe word Solvesso is a registered Trade Mark.

The suspensions prepared above were all smooth, homogeneous and quite stable. In order to test the effect of using these suspensions as coatings for electrical conductors, a 32-mil copper wire containing an outside thin layer of plated cadmium was passed

through each suspension and thereafter into a vertical oven (the effective heated section was about three feet in height) maintained at an air temperature of about 350° to 425° C. The speed with which the conductor was passed through the suspension and the oven varied from about thirty seconds to approximately sixty seconds per pass. Each conductor was passed through the suspension and the oven five times in order to insure a good build-up of the insulating coating. The insulated conductors were then tested for abrasion resistance (using the method disclosed in Copending Application No. 26444/49, Serial No. 659,977), as laid open to public inspection under Section 91 of the Patents Acts 1907 to 1946 also insulation resistance, and dielectric strength. Thermal life measured at 250° C. was of the order of 20 to 30 hours. The following table shows representative results of these tests.

TABLE II.

Suspension No.	Abrasion Resistance Strokes	Insulation Resistance in Mercury	Dielectric Strength (KV)	Build-up Mils
4	7	∞	0.9	2.8
5	14	∞	0.6	2.2
6	12	∞	2.2	2.9
7	13	∞	2.8	2.8
8	7	∞	1.9	2.5
9	13	∞	2.4	2.4
10	26	∞	1.2	1.8
11	4	∞	1.7	3.5
12	3	∞	1.0	2.2
13	2	∞	1.6	2.4
15	22	∞	2.5	2.6
16	11	∞	1.7	2.2
17	25	∞	0.8	3.4

It will, of course, be apparent to those skilled in the art that in addition to the compositions described above, other concentrations of polymeric chlorotrifluoroethylene in the suspension may be employed without departing from the scope of the invention. The various ratios of ingredients which can be advantageously employed have been disclosed previously.

In addition to the active solvents employed above, other such materials may also be used, examples of such solvents being more particularly disclosed in our aforementioned Copending application.

In addition to the known non-solvent diluents employed in the examples above, we may use other oxygen-containing compounds having a boiling point above 50° C. and selected from the class of compounds mentioned in the first paragraph of this specification. Among such compounds may be mentioned, for instance, aliphatic ethers (e.g., diisopropyl ether, di-*n*-butyl ether, dioxane,

tetrahydrofuran, 1,2-di-*n*-butoxy ethane), aliphatic monohydric alcohols (e.g., isobutyl alcohol, *n*-amyl alcohol, isoamyl alcohol, tert-amyl-2-ethyl hexanol, chlorohydrin); saturated aliphatic esters (e.g., methyl acetate, ethyl acetate, ethylene glycol acetate, chloroethyl acetate, beta-methoxy-ethyl acetate, methyl lactate); aliphatic ketones (e.g., acetone, methyl ethyl ketone, methyl-*n*-propyl ketone, diacetone); aliphatic acetals (e.g., dimethyl acetal, 1,3-dioxalane, dichloromethyl formal, bis-beta-methoxyethyl formal); aliphatic lactones (e.g., gamma-butyrolactone, alpha-methyl, gamma-valerolactone); and mixtures of saturated aliphatic monohydric alcohols and dihydric aliphatic alcohols (e.g., including the saturated aliphatic monohydric alcohols mentioned above mixed with, for instance, ethylene glycol, trimethylene glycol, tetramethylene glycol, 2-methyl-2,4-pentanediol, dipropylene glycol). Mixtures of any of the foregoing known solvent diluents may also be employed if desired.

In general, the limit of the number of compounds, both non-solvent and solvent components, is dependent on the limits of miscibility of the components involved in the dispersing phase. Little difficulty has been encountered in using any of the non-solvent components with the solvent components in the dispersing phase.

In general, it is desirable to grind the pulverized solid polymer with the liquid mixture comprising the dispersing phase in a ball mill for several days. However, for purposes of successful application to magnet wire, it may not be necessary to grind for more than 24 to 72 hours, provided the original polymer has been reduced to the order of magnitude of at least 0.2 to 25 microns average particle size before grinding. No heating is necessary at any time for making the suspensions. The time required for ball-mill grinding to give a satisfactory stable suspension may range from about one-half to 15 days or more and, advantageously in the case of the examples described above, from about 1 to 10 days.

The suspensions of polymeric chlorotrifluoroethylene described above may be employed in various ways. They may be used for coating and impregnating various fillers and fabrics; for example, glass cloth, glass batting, asbestos cloth, and mica. If desired, the suspensions may be advantageously employed in making moulding compositions by adding to the suspension various inert inorganic fillers to obtain a homogeneous mixture and thereafter removing the solvent and non-solvent (i.e., oxygen-containing) components of the dispersing phase from the mixture. Laminated products may also be prepared by coating and impregnating sheet material and superposing layers of the impregnated and coated material and pressing the total assembly under heat and pressure to obtain fusing of the polymer and to give a homogeneous article. In some coating applications as, for instance, in the coating of electrical conductors, such as magnet wire, it has been found advantageous to add varying amounts, for example, from one to ten per cent., by weight, or more of a finely ground pigment or filler to the suspensions. Among such pigments and fillers which may be employed are, for example, catalpa clay, bentonite, mica dust, titanium dioxide, silica, lead silicate, and lead titanate.

The suspensions containing active solvents are relatively easy to use, and give products having good appearance, and a high degree of clarity. Films (e.g., no strength temperatures of from 240° to 270° C.) deposited from these suspensions on glass, for example, were clear, completely fused, continuous, and strongly adherent at a maximum fusion temperature of 260° C.

The suspensions have been found to be eminently suitable for treating terratex

(bentonite-asbestos films) for increasing the strength of the latter. More particularly, the strength of terratex, which normally has a tensile of about 240 to 300 psi, was improved to a crosswise tensile strength 1000 psi., and a lengthwise tensile strength of 1400 psi. when about 52%, by weight, polymer based on the weight of the terratex, was added by dipping the terratex in the suspension and baking in an oven.

What we claim is:—

1. A coating composition which is a liquid suspension consisting of (1) a dispersed phase comprising finely divided solid polymeric chlorotrifluoroethylene and (2) a dispersing medium for (1) comprising (a) an organic liquid mixture which includes a low polymer of chlorotrifluoroethylene and which is a solvent for the polymer at elevated temperatures but below the boiling point of the liquid and (b) a non-solvent, liquid, oxygen-containing diluent having a boiling point above 50° C. and selected from the following:—aliphatic ethers (both straight-chained and cyclic), saturated aliphatic monohydric alcohols (including halogenated alcohols) aliphatic ketones, aliphatic esters, aliphatic lactones, aliphatic acetals, mixtures of monohydric saturated aliphatic alcohols and dihydric saturated aliphatic alcohols, and mixtures of all the foregoing oxygen-containing compounds.

2. A coating composition as claimed in claim 1, in which the dispersing medium comprises (a) a low polymer of chlorotrifluoroethylene and alpha-fluoronaphthalene and (b) *n*-butanol.

3. A coating composition as claimed in claim 1, in which the dispersing medium comprises (a) a low polymer of chlorotrifluoroethylene and alpha-chloronaphthalene and (b) *n*-butanol.

4. A coating composition as claimed in claim 1, in which the dispersing medium comprises (a) a low polymer of chlorotrifluoroethylene and mesitylene and (b) *n*-butanol.

5. A coating composition as claimed in claim 1, in which the dispersing medium comprises (a) a low polymer of chlorotrifluoroethylene and alpha-fluoronaphthalene and (b) 2-ethylhexanol.

6. A coating composition as claimed in claim 1, in which the dispersing medium comprises (a) a low polymer of chlorotrifluoroethylene and tert.-butylbenzene and (b) *n*-butanol.

7. The method of making a coating composition which comprises (1) forming a mixture of ingredients comprising (a) finely divided polymeric chlorotrifluoroethylene and (b) a dispersing medium for (a) comprising (A) an organic liquid mixture which includes a low polymer of chlorotrifluoroethylene and which is a solvent for the polymer at elevated temperatures but below the boiling point of the liquid and (B) a non-solvent, liquid,

oxygen-containing diluent having a boiling point above 50° C., selected from the compounds specified in claim 1, and (2) grinding the aforementioned mixture of ingredients
5 until a stable suspension is obtained.

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